ART 34 AMDT

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Claims (revised)

1. A material for manufacture of structural components, excluding electrodes, in a cell for electrolytic reduction of alumina to aluminium,

characterised by

the formula

$(A'_{1-u}A''_{u})_{x}(B'_{1-v}B''_{v})_{y}(C'_{1-w}C''_{w})_{z}O_{t}$,

in which t is essentially 1, 3 or 4, O is the element oxygen, A' and A" are elements from the group Co, Ni, or Zn, B' and B" are elements from the group Al, Cr, Mn, or Fe and C' and C" are the elements Ti or Sn, $0 \leq u < 1$, $0 \leq v < 1$, $0 \leq w < 1$, $1 \leq x \leq 2$, $0 \leq y \leq 2$, $0 \leq z \leq 1$; when t is essentially 1, y = 0 and z = 0, when t is essentially 3, y = 0, w = 0 and C' denotes the element Ti.

2. A material in accordance with claim 1,

characterised in that

the cation A' is essentially divalent Ni, u is essentially 0 and x is essentially 1.

3. A material in accordance with claim 1,

characterised in that

the cation B' is essentially trivalent Al, the cation B" is essentially trivalent Fe and y is essentially 2.

4. A material in accordance with claim 1,

characterised in that

the cation A' is essentially divalent Ni, the cation B' is essentially tetravalent Ti, and u, v and z are essentially 0.

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oxidizing regions of an aluminium electrowinning cell based on substantially inert electrodes.

Summary of the Invention

The invention is the conclusion of an extensive search for materials capable of fulfilling the requirements for a material for structural cell components in oxidizing regions of an aluminium electrowinning cell based on substantially inert electrodes. The stability requirements of such a material are similar to those of an inert anode in said electrowinning cell. In the not yet published Norwegian Patent Application No. 2001-0928 the choice of possible element oxides for an inert anode is narrowed to: TiO_2, Cr_2O_3, Fe_2O_3, Mn_2O_3, CoO, NiO, CuO, ZnO, Al_2O_3, Ga_2O_3, ZrO_2, SnO_2 and HfO_2. The main requirements for a material intended for use in structural cell components are stability at 1 bar oxygen pressure at temperatures above 680°C and a low solubility in the molten electrolyte. The electrical properties are less important, but its electrical conductivity should be far less that the electrical conductivity of the electrodes and the electrolyte. The material should either itself fulfil the requirements, or it should upon contact with the molten electrolyte react to form a surface layer of an aluminate that fulfils the said requirements. Based on solubility considerations, CuO, Ga_2O_3, ZrO_2 and HfO_2 are eliminated from the list of possible element oxides, and we are left with: TiO_2, Cr_2O_3, Fe_2O_3, Mn_2O_3, CoO, NiO, ZnO, Al_2O_3, and SnO_2.

The evaluation leads to a family of materials that can be expressed by the formula

$$(A'_{1-u}A''_u)_x(B'_{1-v}B''_v)_y(C'_{1-w}C''_w)_zO_t$$

in which A' and A" are elements from the group Co, Ni, or Zn, B' and B" are elements from the group Al, Cr, Mn, or Fe, and C' and C" are the elements Ti or Sn. O is the element oxygen. $0 \leq u < 1$, $0 \leq v < 1$, $0 \leq w < 1$ $1 \leq x \leq 2$, $0 \leq y \leq 2$, $0 \leq z \leq 1$, and t is a number that renders the composition charge neutral.

Within this group of oxides, materials most commonly crystallize in the spinel, ilmenite or rock salt structures. In materials of the present invention that possess the

spinel structure, $x+y+z = 3$, $2x + 3y + 4z = 8$, and $t = 4$. In materials of the present invention that possess the ilmenite structure, $x + y + z = 2$, $2x + 3y + 4z = 6$ and $t = 3$. In materials of the present invention that possess the rock salt structure, $x = 1$, $y = z = 0$, and $t = 1$.

Detailed Description of the Invention

A material suitable as an essentially inert material for structural components in the oxidizing regions of a cell for the electrolytic production of aluminium from alumina dissolved in an essentially fluoride based electrolyte where cryolite is an important ingredient, must be resistant to oxidation and dissolution in the electrolyte. A selection of the element oxides which a material for structural components can consist of, was performed based on the following criteria:

-not a gas or having a high vapour pressure at process temperature

-not converted by cryolite or AlF_3 in the cryolitic mixture, i.e. a large positive value of ΔG° for the reaction between the element oxide and AlF_3 to form the element fluoride and aluminium oxide (reaction 1).

$$MO_x + 2x/3AlF_3 = MF_{2x} + 2x/6Al_2O_3 \qquad (1)$$

-not converted by alumina, i.e. not a negative value of ΔG° for the reaction between the element oxide aluminium oxide and sodium fluoride to form a sodium element oxide and aluminium fluoride (reaction 2)

$$MO_x + 6yNaF + yAl_2O_3 = Na_{6y}MO_{x+3y} + 2yAlF_3 \qquad (2)$$

Of elements with the normal valence 2, the only possible elements are thus Co, Ni, Cu and Zn. Of elements with valence 3 one is left with only the elements Cr, Mn, Fe, Ga and Al. Of elements with valence 4 one is left with only the elements Ti, Zr, Hf, Ge and Sn. Cu, Ga, Zr, Hf and Ge may be eliminated from the list based on solubility considerations, and we are left with the following list of elements: Co, Ni, Zn, Al, Cr, Mn, Fe, Ti and Sn. The possible materials for structural cell components in an

aluminium electrowinning cell based on substantially inert electrodes are thus limited to the oxides of the listed elements, or combinations of these oxides in mixed oxide compounds.

The materials within this group can be expressed by the formula:

$$(A'_{1-u}A''_{u})_{x}(B'_{1-v}B''_{v})_{y}(C'_{1-w}C''_{w})_{z}O_{t} \qquad \text{(a)}$$

in which A' and A" are divalent elements from the group Co, Ni, or Zn, B' and B" are trivalent elements from the group Al, Cr, Mn, or Fe, and C' and C" are the tetravalent elements Ti or Sn. O is the element oxygen. $0 \leq u < 1$, $0 \leq v < 1$, $0 \leq w < 1$ $1 \leq x \leq 2$, $0 \leq y \leq 2$, $0 \leq z \leq 1$, and t is a number that renders the composition charge neutral.

Under favourable conditions the divalent oxides NiO, CoO and ZnO all react with alumina to form an essentially insoluble surface aluminate layer (reaction 3).

$$AO(s) + Al_2O_3\ (diss) = AAl_2O_4\ (s) \qquad (3)$$

where A = Co, Ni, Zn. Therefore, CoO, NiO and ZnO and solid solutions of these form one group of possible materials for structural cell components. These compositions are expressed by formula (a) with x = 1, y = z = 0, and t =1. This is further illustrated in Examples 1 and 2.

Compounds of di- and trivalent element oxides will in this case be of the spinel structure. Spinels like $NiFe_2O_4$, $CoFe_2O_4$, $NiCr_2O_4$ and $CoCr_2O_4$ have been suggested and extensively tested as candidates for inert anodes. In these materials, Al from the molten electrolyte has been observed to exchange with the trivalent cation to form essentially insoluble, insulating solid solutions of the type $Ni(B'_{1-v}Al_v)_2O_4$, where $0<v<1$, B' = Fe, Cr, Mn. This is further illustrated in Examples 3, 4, and 6. These materials are thus possible materials for structural cell components. The pure aluminates $NiAl_2O_4$, $CoAl_2O_4$ and $ZnAl_2O_4$ are also possible materials for structural cell components.

One compound of di- and tetravalent element oxides, Zn_2SnO_4, forms a spinel oxide. This material may in principle be used for structural cell components.

Other stable spinel compositions that are possible materials for structural components of an aluminium electrowinning cell are achieved by substituting a divalent/trivalent spinel with a tetravalent oxide, while simultaneously adjusting the contents of the divalent and trivalent oxides in order to maintain the site and charge balance requirements of the spinel structure. This embodiment of the present invention is exemplified in Example 5.

Spinel type materials thus form another subset of materials for structural components of aluminium electrowinning cells. These compositions are expressed by formula (a), with $x + y + z = 3$, $2x + 3y + 4z = 8$, and $t = 4$.

$NiTiO_3$, $CoTiO_3$ and solid solutions of these crystallize with the ilmenite structure. A cell material with the ilmenite structure may also be obtained by substitution of a trivalent element from the list of possible elements for equimolar amounts of divalent and tetravalent elements. These compositions are expressed by formula (a) with $x + y + z = 3$, $2x + 3y + 4z = 6$, and $t = 3$.